RESEARCH ARTICLE

Preparation and Testing of Bast Fiber Reinforced Thermoplastic Composites under Chemical Treatment

Haydar U. Zaman*[1], Ruhul A. Khan[2]

[1]National University of Bangladesh and Institute of Radiation and Polymer Technology, Bangladesh Atomic Energy Commission, Savar, Dhaka, Bangladesh
[2]Institute of Radiation and Polymer Technology, Bangladesh Atomic Energy Commission, Savar, Dhaka, Bangladesh

ABSTRACT: Thermoplastic polypropylene (PP) composites containing 10, 20, 30, and 40% wt% of calotropis gigantea fiber (CGF) were created in the current study using compression molding in the presence of alkaline pretreated CGF (ACGF), which was modified with aminopropyltrimethoxy silane (ACGF/AS) and tetramethoxyorthosilicate (ACGF/TS) as a silane coupling agent. The composites' CGF content has been tuned, and a 40 weight percent CGF content exhibited the optimum mechanical performance. In comparison to virgin PP, composites containing 40% CGF increased their impact strength and tensile strength by 225.4% and 54.2%, respectively, but only 39% when using 30% CGF. After alkali pretreatment, silane is added to CGF/PP composites to improve the mechanical properties, which in turn cause the composites to absorb water. The increase in CGF content has made this tendency more obvious. When compared to CGF/PP composites, which demonstrated 18% tensile modulus and 59% impact strength, ACGF/TS/PP composites showed maximal mechanical characteristics at 40 wt% CGF content, while CGF/PP composites only managed 20% tensile strength at 30% CGF content. To find out more about fiber-matrix adhesion, SEM revealed enhanced adhesion between CGF and PP following silane modification. The horizontal combustion rate was dramatically lowered by adding $Mg(OH)_2$ to ACGF/AS/PP and ACGF/TS/PP. According to DSC data, adding AS and TS to CGF increased the crystallinity, melting, and crystallization of the composites. Compared to ACGF/AS/PP and ACGF/PP composite, ACGF/TS/PP composite had a superior thermal stability.

KEYWORDS: Bhendi fiber for textile, composites, natural fiber, agricultural waste, mechanical properties.

INTRODUCTION

Natural fiber composites (NFs) have recently seen a significant increase in interest [1-5]. Due to their high toughness, high specific characteristics, light weight, recyclability, low cost, and "eco-friendliness," NFs including vetiver, calotropis gigantea, abaca, snake grass, etc. are currently widely employed to produce composites [6, 7]. Hydrophobic thermoplastics are inherently incompatible with these fibers. Plant fiber reinforced thermoplastic composites, despite significant flaws in industrial packaging and performance for sheet work, fences, furniture, and building, are becoming more and more appealing [8, 9]. Haydar and colleagues' extensive study on NF composites has shown that they are a fantastic alternative to synthetic materials [10-14].

Calotropis gigantea fiber (CGF) is known as bast fiber. We selected CGF because it is an oil-absorbing component used in the oil separation process to remove oil from water and has suitable buoyancy, hydrophobic-oleophilic properties, a high oil absorption capacity, and an oil-water separation efficiency. CGF inhabits China, India, Bangladesh, among other countries, and is a member of the *Asclepiadaceae* family. As a raw material with inherent biodegradability, CGF is mostly used in the textile industry. Calotropis produces a hardy fabric that can be used for fishing nets, ropes, carpets, and sewing thread. This tree can reach heights of 3 to 5 meters and produces clusters of waxy blooms. It also has milky-tasting stalks with oval-shaped pale green leaves that are further supplemented by fibers. For the creation of composite materials, the fibers extracted from the CG plant's stems are employed. Extract CG bark fiber has a composition of 73.8 percent

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cellulose, 20.5 percent hemicellulose, 2.7% lignin, and 1.18% waxy compounds [15]. Chemical element performance plays a crucial role in determining the mechanical characteristics of the fiber in the NF composite when choosing new fibers. The chemical elements of NFs that are already utilized as reinforcements in NF composites with CG fibers are listed in Table 1. Even though cellulose fibers have many advantages, they lessen the negative effects of high temperatures and the prevalence of moisture absorption. In order to create various hydrogen bonds and CGFs to create hydrophilic, hydroxyl groups stand in for cellulose. Due to flaws in the plastic material and fiber, manufactured composites, such as polar (hydrophilic) NFs and nonpolar (hydrophobic) thermoplastic matrix, lose mechanical properties [16].

Scientists from all over the world have paid close attention to composites that use CGF as a reinforcing fiber in the thermosetting resin matrix because of the potential for plants to evolve [17, 18]. The advantages of thermoplastic composites over thermoset composites are numerous. Higher fracture strength, improved solvent resistance, reusability, and quick, fresh, automatic processing are a few of them [19]. The main appeal of thermoplastic composites is their potential for rapid decomposition as no chemical reaction is required. The mechanical characteristics of the composite significantly change when NF is added to the matrix. The filler's composition, size, and degree of interfacial bond with the matrix influence the composite's physical characteristics and the factors that contribute to the increase in mechanical strength [20]. Therefore, a key factor in enhancing the filler-matrix interface adhesion is making the appropriate filler selection for a given matrix.

Because of its remarkable qualities, including transparency, superior surface strength, high impact strength, high thermal distortion temperature, and dimensional stability, PP was chosen as the study's thermoplastic resin. Additionally, PP is excellent for blending, strengthening, and filling. In comparison to other thermoplastics, PP has a higher toughness and higher melting point (160°-170°C) and softening points (over 149°C). It has a unique mix of exceptional mechanical, thermal, electrical, and chemical properties. It is a fantastic component for electrical applications because of the good adjustment of respectable thermal features, minimal humidity pickup, and respectable dielectric features. The most promising method for producing PP composites with natural polymer fibers derived from biomass [21-23]. While synthetic polymers are hydrophobic, NFs are hydrophilic. NFs are frequently prevented from serving as fillers by poor distribution, insufficient strength, and low mechanical characteristics, which are all followed by poor bonding between the NF and the matrix [21, 22]. For the ultimate application of the composite components of NFs, the coupling agent must be added to or chemically changed. Chemical treatments are one of the most efficient techniques to give composites their physical qualities. The compounds can efficiently interact with cellulose and activate the hydroxyl group, inducing the properties the polymer needs. To strengthen the connection between these two different surfaces, alkali pre-treatment and subsequent silane treatment were utilized [24]. The swelling of cellulose fibers is impacted by alkali treatment, which causes cellulose to change its structure to one that is thermodynamically more stable than the original structure [25]. Alkali-treated wood fibers' subsequent chemical treatment with silane would improve the fibers' adherence to the polymer matrix in wood plastic composites [26-29]. By the creation of silanol (Si-OH) and the formation of bonds between siloxane (Si-O-Si) and natural fibers, the hydrophilic surface of the wood fibers is changed to a hydrophobic surface at this stage [30]. Additionally, it is expected that silane treatment may result in simpler polymer melt dispersion amongst CGF, increase processability, and reduce CGF damage from shear stresses during compounding process. PP-based AS and TS-treated composites with CGF reinforcement have not yet been released, according to a thorough examination of the literature. Therefore, the utilization of AS and TS as coupling agents for creating CGF/PP composites has been investigated in this study. This paper looked into how CGF/PP composites' physico-mechanical, morphological, and thermal characteristics were impacted by chemical treatment and fiber content.

EXPERIMENTAL
Materials
Calotropis gigantea was discovered in isolated regions of Bangladesh. The liquid detergent was purchased in Chennai, India. The diameter of the CGF was 0.22 ± 0.055 mm. Isotactic PP

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(M110) matrix component with 0.9 g/cc and MFI 11g/10 min was purchased from M/s Haldia Petrochemicals in Calcutta, India. Tetramethoxyorthosilicate (TS, 99%) and aminopropyltrimethoxy silane (AS, 97%) were purchased from E. Merck in Darmstadt, Germany, and used for chemical processing. Other chemicals, such as pure methanol and NaOH, were procured from Aldrich Chemical Co. Inc., while magnesium hydroxide ($Mg(OH)_2$), a flame retardant, was purchased from Sigma-Aldrich (USA).

METHODS

A CG plant that is more than a year old appears to be ideal for fiber extraction. The tree's leaves, including the stalks, were removed, and the stems were pruned to the appropriate length. After drying for three days at room temperature, the steams were then manually removed using a decorticated process. Figure 1 shows the CG plant and the fibers that were harvested. Table 1 provided information on the properties of CG fiber. The CGF was isolated from unwanted components, then make a 140 mm cut of the same size. To eliminate foreign materials, well-drained CGFs were washed for an hour with a detergent solution (2%) before being rinsed with pure water. To regulate the humidity (1-2%), the fibers were dried at 60°C for 24 hours before being put in a vacuum desiccator. An analytical electrical balance was used to weigh the prepared sample.

Figure 1: (a) CG plant (b) stems and (c) raw CGF extracts

Table1. Features of CG fiber

Description	values
Physical properties	
Density (g/cc)	1.360
Diameter (μm)	90-260
Chemical compositions	
Cellulose (%)	73.8
Hemicellulose (%)	20.5
Lignin (%)	2.7
Wax (%)	1.18
Mechanical properties	
Tensile strength (N)	7.95
Percentage of elongation (%)	5.03

Pretreatment of CGF

CGFs were put in a tray after being washed and dried. The CGFs were submerged in a tray filled with a 5% alkali solution for roughly an hour at room temperature. When a stronger alkaline response of the water was detected, all NaOHs were then removed and rinsed in pure water. The last load of washing was then finished with 3% acetic acid to neutralize the remaining NaOH.

Chemical Treatments

Chemical treatments using tetramethoxyortho silicate (TS) and aminopropyltrimethoxy silane (AS) were performed on alkaline-pretreated CGFs. By combining AS or TS in a mixture of methanol and water (50:50) for one hour, a 3 weight percent solution of silane was created. At room temperature, alkaline-pretreated CGFs were submerged in this solution for one hour. Following the coupling reaction, the CGFs were

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dehydrated at 70°C and kept at a steady weight for 30 hours in a vacuum oven.

Preparation of Composites

In a parallel arrangement, dry CGFs were attached together with adhesive tape and molded between PP sheets. By stacking films, untreated and treated CGF (10–40 wt%) composites were created using a hot press.

machine. By pressing this stacking at 180°C for 5 minutes while maintaining a constant 10 MPa pressure, composites were created. The mold was then taken out of the press, safely sandwiched between two steel mold plates, and the final one was swiftly put out with ice water. Figure 2 shows a diagram of the manufactured composite. Table 2 displays the compositions of the control and modified CGF/PP composites.
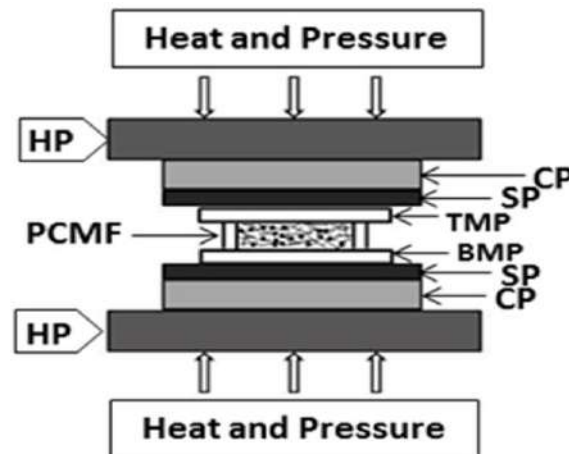
NB: HP-Hot press platen, PCME-Mixture of PP and CGF in a mold frame, CP-Conduction plate, SP-Steel plate, TMP-Top mold plates, BMP-Bottom mold plates
Figure 2: Schematic representation of the hot press used to fabricate composite plates.

Table 2: Compositions of untreated and treated CGF/PP composites

Ingredients (phr)	Sample designation			
	CGF/PP	ACGF/PP	ACGF/AS/PP	ACGF/TS/PP
PP	100	100	100	100
CGF	0, 10, 20, 30, 40	–	–	–
Alkalized CGF	–	0, 10, 20, 30, 40	–	–
AS treated ACGF	–	–	0, 10, 20, 30, 40	–
TS treated ACGF		–	–	0, 10, 20, 30, 40
Ingredients (phr)	CGF/FR/PP	ACGF/FR/PP	ACGF/AS/FR/PP	ACGF/TS/FR/PP
PP	100	100	100	100
CGF	0, 30	–	–	–
Alkalized CGF	–	0,30	–	–
AS treated ACGF	–	–	0, 30	–
TS treated ACGF	–	–	–	0,30
$Mg(OH)_2$	10	10	10	10

CGF: Calotropis gigantea fiber; FR: Fire retardant

Mechanical Measurement of Composites

Shimadzu UTM (model AG-1, Japan) tensile tests for composites were carried out in accordance with ASTM-D 638-03 at a crosshead speed of 10 mm/min and a gauge length of 20

mm. Izod Impact test was carried out in accordance with ASTM-D 256 using an impact machine (model, Toyo Seiki Co., Japan). A sample for impact testing had the following measurements: 63.5 mm × 3 mm × 12.7 mm.

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Room temperature (27°C ± 3°C) and relative humidity of 50 ± 3% were the conditions for all testing. The values were the mean of five measurements.

Morphological Properties

Using a scanning electron microscope (SEM, model JEOL JSM-5310) operating at 20 kV, the morphology of the tensile fracture surface of untreated and treated composites was examined. To prevent the buildup of electrical charge before to SEM, samples were coated with a thin coating of gold (25 nm) using a BALTEC SCD 050 sputter coater.

Flammability Test

Using horizontal-vertical flame chamber equipment, a horizontal combustion test in accordance with ASTM D635 was used to identify sample combustion (Atlas, HVUL). In the horizontal flame test, the sample was laid out horizontally and a fire started on one end of it using natural gas. The following countenance was used to determine the combustion rate (1):

$$B_r = 60l/t \quad ----(1)$$

where B_r is the combustion rate in mm/min, is the length of the burn travel and t is the time in second for burn travel. A minimum of five measurements were recorded in each specimen.

Thermal Properties

A DSC (DSC, Perkin Elmer DSC-7) was used to measure the thermal parameters of composite materials, including their crystallization temperature, melting temperature, and melting enthalpy. Each sample (5–10 mg) was heated in an aluminum pan from 30°C to 250°C at a heating rate of 10°C/min, and then kept at 250°C to verify a duplicate thermal history. From the initial heating scan, the T_c, T_m, ΔH_m, and crystallinity (X_c) were measured. X_c was decided based on the following expression (2):

$$X_c(\%) = \frac{\Delta H_m}{\Delta H_{m(crys)}} \times 100 \quad (2)$$

where ΔH_m is a specimen's melting enthalpy and is equal to the 138 J/g melting enthalpy of pure PP crystal [31]. A Perkin Elmer Thermogravimetric analyzer (TGA; Waltham, Massachusetts, USA) was used to quantify the thermal degradation of composite materials under the following conditions: 5–10 mg of specimens, a heating rate of 20°C/min, a temperature range of 25–600°C, and an airflow rate of 20 mL/min.

Water Absorption Evaluation

Water absorption tests were conducted using untreated and treated CGF/PP composites. Specimens were exposed to distilled water at a temperature of 25°C after being dried at 70°C and regularly removed from the water until they reached a constant weight. The specimens were weighed after the surface water had been cleaned off using a clean cloth. The amount of water absorbed was calculated as follows:

$$\text{Water absorption (\%)} = \frac{W_2 - W_1}{W_1} \times 100$$

where W_1 and W_2 are the specimen's initial and post-soaking weights, respectively.

RESULTS AND DISCUSSION
Tensile Properties

The tensile strength of control and treated CGF/PP composite samples measured against CGF content is shown in Figure 3(A). As can be seen, the tensile strength of the CGF/PP composite increases gradually as CGF percentage rises up to 30 wt% before decreasing as CGF concentration rises. The tensile strength increases with CGF content, according to previous studies [32].

The transfer of even stress from the matrix to the fiber is largely attributed to this phenomenon. Composites with a low filler concentration (10 wt%) have poor tensile qualities because of their low CGF content, population, and capacity for load transfer between them. As a result, only very small strains occur in the PP and tension is deposited at specific locations in the composites. The CGF population is optimal for maximum adaptation and the fiber actively contributes to tension transmission at a 30 wt% CGF loading level. The composite has poor tensile characteristics because of the weaker adhesion between CGF and PP and the increased filler loading (40 wt%). At this point, the PP matrix's fiber aggregation causes non-uniform stress transfer that eventually results in the creation of microcracks, which results in a weak interfacial interaction between PP and CGF.
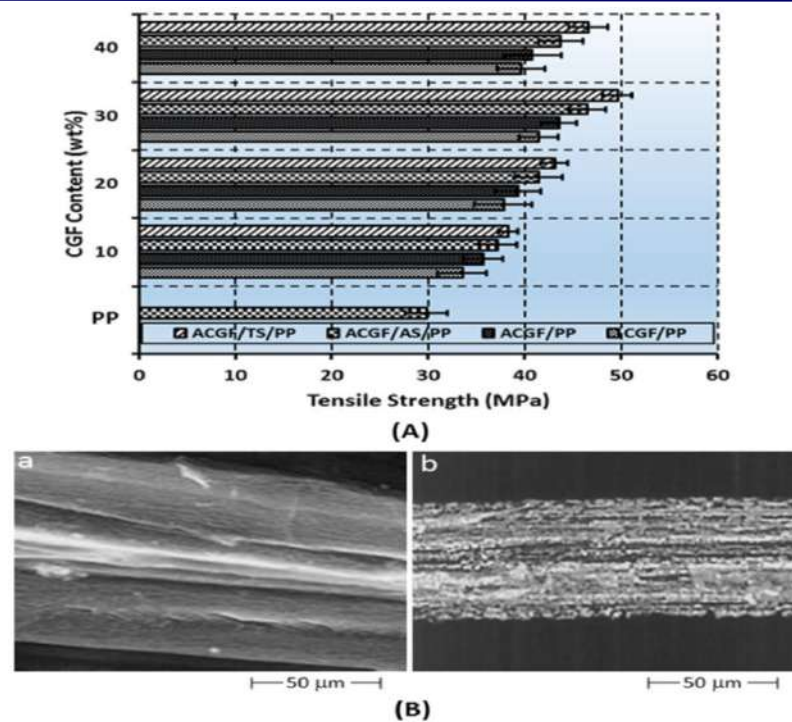
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Figure 3: (A) Tensile strength of CGF/PP, ACGF/PP, ACGF/AS/PP, and ACGF/TS/PP composite samples; and (B) SEM micrographs of CGF

Figure 3(A) depicts the relationship between tensile strength and CGF content both with and without alkali pretreatment silane treatment. In comparison to the 30 wt% CGF/PP composite, it was discovered that the tensile strength of the ACGF/PP, ACGF/AS/PP, and ACGF/TS/PP composites rose by 5%, 12.3%, and 19.8%, respectively. For the ACGF/PP sample, CGF improved microporosity with a lot of holes and cavities on the surface and boosted tensile strength by removing natural and synthetic impurities (such as lignin, hemicellulose, and wax & oils) that covered the external surface of the fiber cell wall. The SEM picture (Fig. 3B, a) shows that the surface of CGF has pores. Through the removal of soluble components including hemicellulose, tylose, and other fatty acids, alkali treatment widens these pores (Fig. 3B, b). The CGF's surface area increases as a result of the pores' expansion, and improvements in the fiber-to-shape ratio and the interfacial bonds between the CGF and PP that follow increase the material's mechanical properties. Through mecerization, more potentially reactive sites can be created, which improves fiber soaking. Additionally, mercerization reduces the fiber's diameter while increasing its form ratio, which improves the uneven surface structure, the fine fiber-matrix interface binding, and the mechanical properties [33].

Tensile strength of alkaline pretreatment silane (3 wt% AS or TS) treated CGF/PP composites considerably increased as CGF load levels increased from 10 to 30 wt%, and increased by 12.3% and 19.8%, respectively, compared to the 30 wt% CGF/PP composites. First, CGF extraction through alkali pretreatment, which modifies the surface characteristics of CGF, may be related to increased tensile strength. Second, silanization can be used to reliably produce silanols by hydrolyzing silane, condensing silanols, and forming linkages between siloxane and CGF (Fig. 4(a) and 4(b)).

According to theories, silane action can make it simple for PP to distribute throughout CGF, increase processability, and lessen CGF loss due to shear stress during composite processing. The four methoxy groups of TS can form silanols by hydrolysis, whereas the three methoxy groups of AS can form silanols by hydrolysis. As a result, TS is better than AS in producing a stronger silane crystal complex with CGF. Additionally, the AS aminopropyl group can be more hydrophilic than the TS one. Therefore, TS and PP are more compatible than AS. It shows how effectively silane activity can strengthen CGF/PP bonds, enhancing the composite's tensile strength.
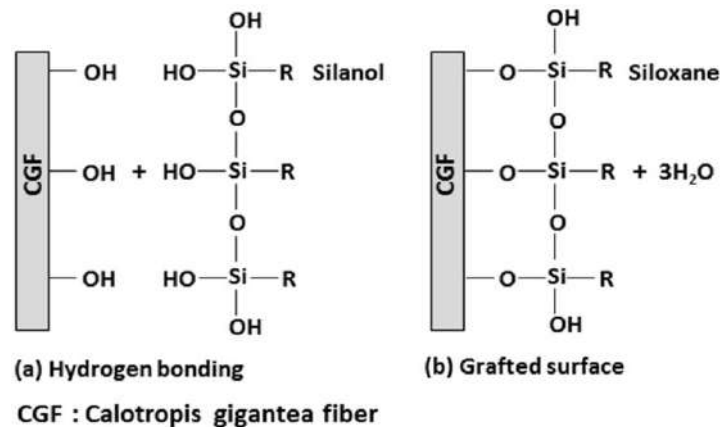
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Figure 4: Bonding between silane and calotropis gigantea fibers (a) hydrogen bonding (b) the grafted surface

Figure 5(a) depicts the relationship between tensile modulus (TM) and CGF concentration both with and without alkali pretreatment silane treatment. When compared to virgin PP, the TM of composites containing 40 weight percent of CGF rose by 225.4, 240, 262.4, and 283.6%, respectively, for CGF/PP, ACGF/PP, ACGF/AS/PP, and ACGF/TS/PP. The TM's CGF content was used in its development [34, 35]. Because of the CGF content, the growth in TM can be further closely connected with the growth in the stiffness of the composite [36]. Compared to control composites, treated composites (ACGF/PP, ACGF/AS/PP, and ACGF/TS/PP) exhibit greater TM. It was discovered that, as compared to the control sample, the TM of the composites with a 40 weight percent CGF content of ACGF/PP, ACGF/AS/PP, and ACGF/TS/PP rose by 4.5%, 11.4%, and 17.8%, respectively. Because there are some significant chemical connections between the hydrophobic portion of the silane on the CGF surface and PP, it has been found that ACGF/TS/PP composites exhibit better TM than other composites.
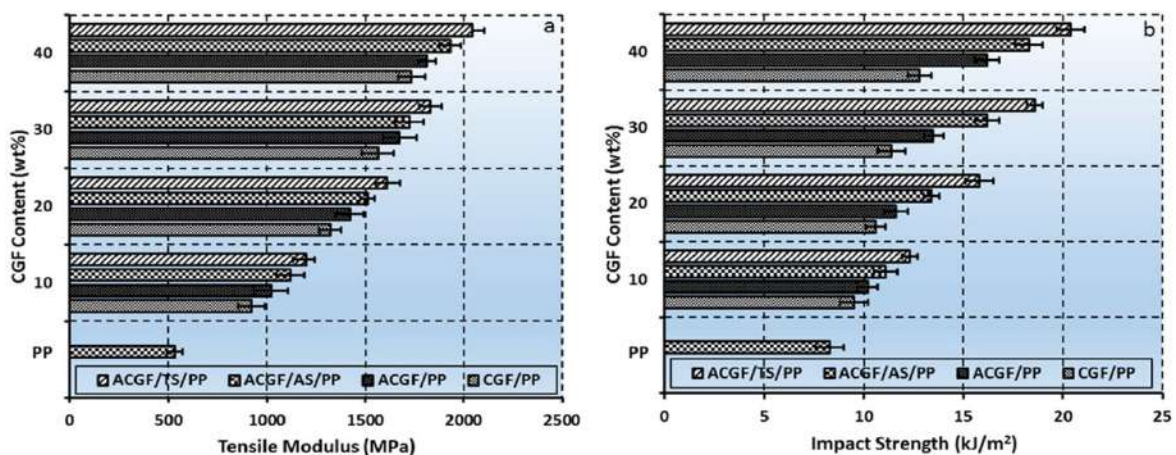

Figure 5: (a) Tensile modulus and (b) impact strength of CGF/PP, ACGF/PP, ACGF/AS/PP, and ACGF/TS/PP composites.

Impact Properties

The three treatments' effects on the CGF/PP composite's Izod impact strength are depicted in Figure 5(b). The impact strength of ACGF/PP, ACGF/AS/PP, and ACGF/TS/PP composites was 26.5%, 42.9%, and 59.4% higher than CGF/PP composites at a loading level of 40 wt% CGF. These findings are accurate because there was a strong interfacial contact between CGF and PP, which allowed CGF to absorb energy. A stronger force is required to extract the CGF shots as the CGF content rises. The impact strength consequently rises as a result. When compared to the control sample, the treated composites had higher impact strength values. The ideal interaction between the treated CGF and PP matrix was responsible for the higher impact strength of the ACGF/AS/PP and ACGF/TS/PP composites. The lack of CGF pullout and fiber

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aggregation in the control sample may be the cause of its weak impact resistance.

Rockwell Hardness Properties of Composites

Figure 6 shows how CGF content affects the Rockwell hardness of composites made of CGF/PP, ACGF/PP, ACGF/AS/PP, and ACGF/TS/PP. Generally speaking, thermoplastics in composites with fibers that improve modulus have harder thermoplastics.

Increases in CGF content have been seen to increase the hardness of both controlled and treated composites. In inelastic composites, the addition of CGF to PP reduced the chain's flexibility. The hardness of ACGF/PP, ACGF/AS/PP, and ACGF/TS/PP composites was 2.4%, 5.2%, and 7.6% higher than CGF/PP composites at loading levels of 40 wt% CGF content, respectively. As a result, there is stronger intrinsic adhesion between PP and CGF and there is greater CGF dispersion in PP, which decreases the gaps.
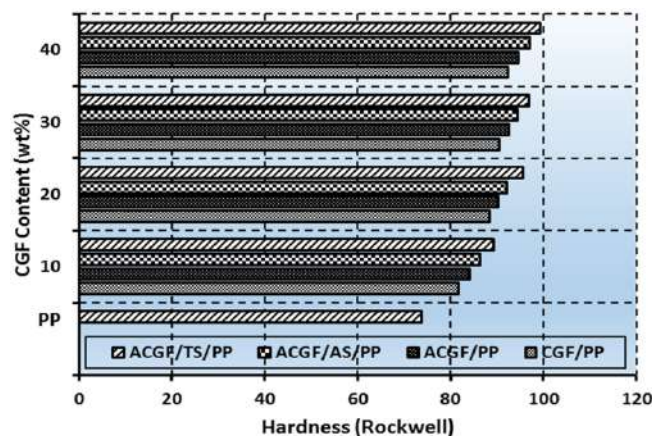

Figure 6: The hardness of CGF/PP, ACGF/PP, ACGF/AS/PP, and ACGF/TS/PP composites

Morphology of Fractured Surfaces

The tensile fracture surfaces of CGF/PP, ACGF/AS/PP, and ACGF/TS/PP composites with a 40% CGF content are shown in Figures 7(a) through (c). In contrast to other treated composites, CGF/PP composites (Fig. 7, a) appear to be isolated from the PP matrix and have a sizable pull-out. These characteristics suggest weak interfacial bonding between CGF and PP and fiber-to-fiber contact. This composite's interface structure does not allow for effective stress transmission. This assertion is consistent with the low tensile strength shown in Figure 3(A). Figure 7(b) shows that the CGFs were considerably pulled out during the fracturing process and that the most PP was adhered to their surface. Compared to CGF/PP composite, the ACGF/AS/PP composite appears to have less fiber pullout. As a result, CGF and PP now have a strong interface bond. When it comes to ACGF/TS/PP composites (Fig. 7c), CGFs were partially pulled out during the fracture process, and numerous PPs are still adhered to the CGF's surface. The result shows that PP/ACGF/TS composites have a substantially better interface bonding between CGF and PP than do PP/ACGF/AS composites.
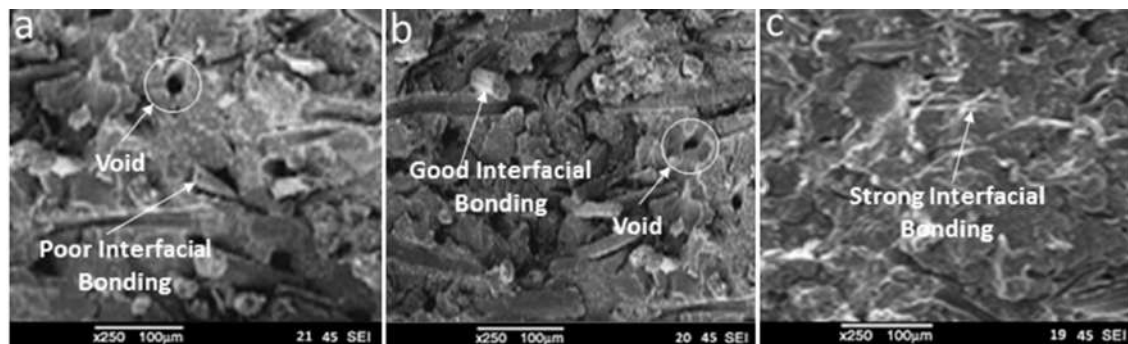

Figure 7: SEM micrographs of (a) CGF/PP (b) ACGF/AS/PP and (c) ACGF/TS/PP composites in 40 wt% CGF content

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Flammability of the Composites

Figure 8 displays the rate of combustion of PP and its composites (control and treatment samples) with and without flame resistance. It was discovered through experimentation that PP, which shows more vulnerability to CGF flame, burns more slowly than CGF/PP composite. $Mg(OH)_2$ has proven to be useful for heavy loads and functions as a fire-resistant for polymers [37]. However, ten weight percent $Mg(OH)_2$ lowers the CGF/FR/PP composite's combustion rate to 29.4 weight percent. By doing this, $Mg(OH)_2$ is guaranteed to operate as a fire-resistant addition and release large amounts of water at high temperatures, reducing the amount of fuel needed to sustain combustion during a fire. Additionally, it is assumed that the fire-resistant additive uses the heat from the ignition zone to produce a char through ignition following greater fire-resistant protection and less smoke production, decreasing the probability of continued igniting. Separately, the flame retardant properties of the ACGF/AS/PP and ACGF/TS/PP composites were greatly improved by the addition of 10% $Mg(OH)_2$. In comparison to ACGF/TS/PP composite, which shown remarkable advancement in fire retardancy with a burning speed of approximately 11.2 mm/min, it was discovered that ACGF/AS/PP composite burned at a moderate rate of 14.3 mm/min. The findings indicated that the flame resistance property of the silane-treated composites was enhanced by the addition of fire retardant.
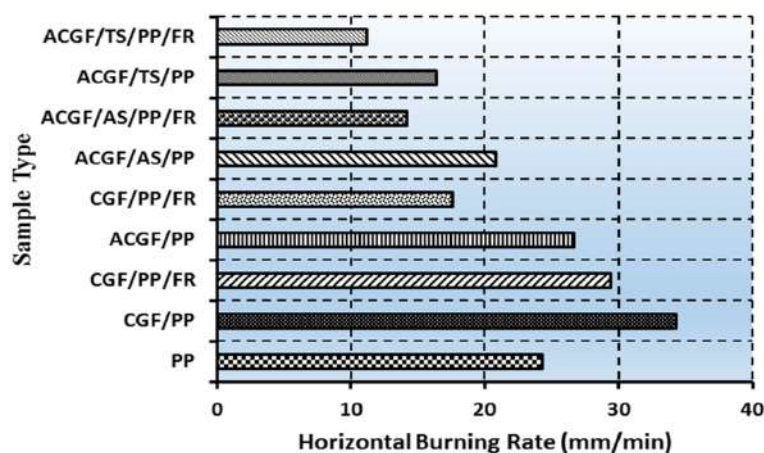

Figure 8: The combustion rate of virgin PP and its composite with and without fire resistance

Thermogravimetric Analysis (TGA)

Figure 9 displays the TGA curves of neat PP, CGF/PP, ACGF/PP, ACGF/AS/PP, and ACGF/TS/PP composite samples. Table 3 provides a list of the degradation temperatures for virgin PP and its composites. For instance, Table 3 shows that the principal decaying temperature (T_{onset}) increased from 270.4°C for virgin PP to 280.3°C for CGF/PP composite with a char residue of 8.2 wt%, demonstrating an improvement in the thermal stability of PP. In a one-step degradation process from 270.4°C to 450.8°C, it has also been noted that the weight of fresh PP drops, and only a very small quantity of PP residue is left in the gaseous products as a result of the PP's thermal deterioration at high temperatures. According to Table 3, the T_{onset} for ACGF/PP composite was approximately 23.1°C higher than PP. However, a two-stage degradation process has been reported for the composites ACGF/AS/PP and ACGF/TS/PP, where weight loss at 262.3°C coincides with CGF deterioration and the second step is indicated by the degradation of the PP at 400°C. The thermal degradation temperatures of the two phases of CGF/PP composites are, nevertheless, quite high in the presence of AS and TS (about 23.4°C and 25.5°C), showing stronger thermal stability than composites without silane. This performance may result from the cross-linking of PP and CGF or from PP's molecular chain extension, which increases molecular weight [38].

Differential Scanning Calorimetry (DSC)

DSC was used to examine the cooling and heating curves of virgin PP and CGF/PP composites with and without coupling agents (Figure 10, a-d). Figure 10(a) shows that the crystallization temperature (T_c) of virgin polypropylene was 117.2°C and that adding 40

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weight percent of CGF to virgin polypropylene resulted in a 1.9°C rise in T_c for composites without coupling agents. This might be because nucleation sites were created while CGF was present. T_c increases to 1.9-7.6°C for ACGF/AS/PP and ACGF/TS/PP composites,

respectively, significantly enhancing the coupling agent-mediated nucleation mechanism The nucleation of the PP matrix created by the inclusion of AS and TS may be enhanced by the ester link between PP and CGF.
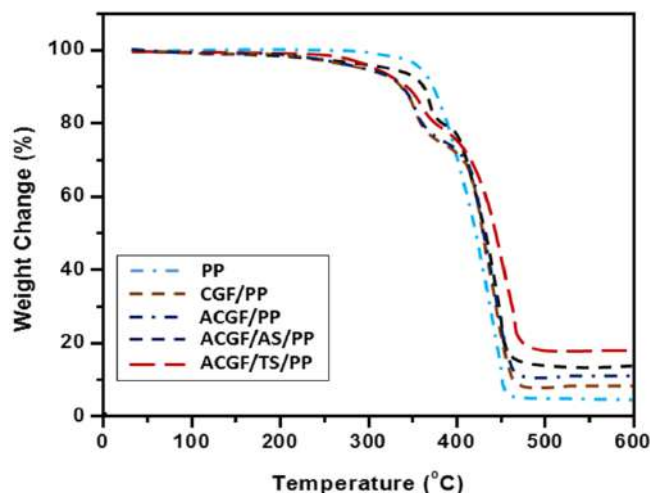

Figure 9: TGA thermograms of neat PP, CGF/PP, ACGF/PP, ACGF/AS/PP, and ACGF/TS/PP composites

Table 3: Thermal degradation temperatures of virgin PP and its composites

Sample	T_{onset} (°C)	$T_{25\%}$(°C)	$T_{60\%}$(C)	Char residue at 600°C (wt%)
PP	270.4	399.5	438.5	4.9
CGF/PP	280.3	390.1	448.1	8.2
ACGF/PP	293.4	393.6	448.3	10.5
ACGF/AS/PP	303.7	402.7	448.7	12.2
ACGF/TS/PP	305.8	404.2	450.8	18.7

Virgin PP had a melting point (T_m) of 165.1°C (Fig. 10, b). The addition of CGF (40 weight percent) raised T_m by approximately 3.6°C in virgin PP. The slight increase in Tm of PP in CGF/PP composites is attributed to fiber-fiber and fiber-polymer interactions, respectively. Additionally, the addition of AS and TS raised the temperature of the CGF/PP samples by 5.7–6.2°C. T_m can be improved by the two substances' compatibility with one another. The melting enthalpy (ΔH_m) of virgin PP was discovered to be 81.3 J/g (Fig. 10, c). The virgin PP's ΔH_m was increased to 93.4°C by the addition of CGF (40 wt%). When AS and TS were added, CGF/PP composites showed greater ΔH_m than CGF/PP composites alone. These findings show that composites containing silane will melt; necessitating more energy in comparison to AS, TS offers a superior ΔH_m for CGF/PP composites.

The value of crystallinity (X_c) rose with the addition of CGF, as seen in Figure 10(d). CGF

raises the degree of crystallization and speeds up the crystallization rate since it serves as the nucleation site for PP. The growing contact between CGF and AS or TS, which slows the matrix's crystallization phase and reduces the degree of crystallization compared to PP/CGF samples, is the cause of the drop in X_c values of ACGF/AS/PP and ACGF/TS/PP composites. However, the intermolecular interaction between PP and CGF is increased when AS or TS are added to CGF. This appears to prevent the PP phase from crystallizing in AS and TS.

Water Absorption (WA)

Figure 11 displays the WA quality results of the CGF/PP, ACGF/PP, ACGF/AS/PP, and ACGF/TS/PP composites as a function of CGF concentration and water soaking duration (24 hours). The WA of the composites is impressed by the significant issues of the immersion period and CGF loading. Due to the enhanced availability of the cellulose -OH group, which

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can absorb water, the WA of PP/40 wt% CGF composites was 15.3% higher than PP/30 wt% CGF composites after the sample had been soaked in water for 24 hours. While the -OH groups on the surface of the CGFs could not be removed by the composites, ACGF/PP offered more WA (1.1%) than ACGF/AS/PP (0.82%) and ACGF/TS/PP (0.69%). Contrarily, silane surface modifications improved the mechanical interlocking between CGF and PP, reducing WA for the composites ACGF/AS/PP and ACGF/TS/PP.
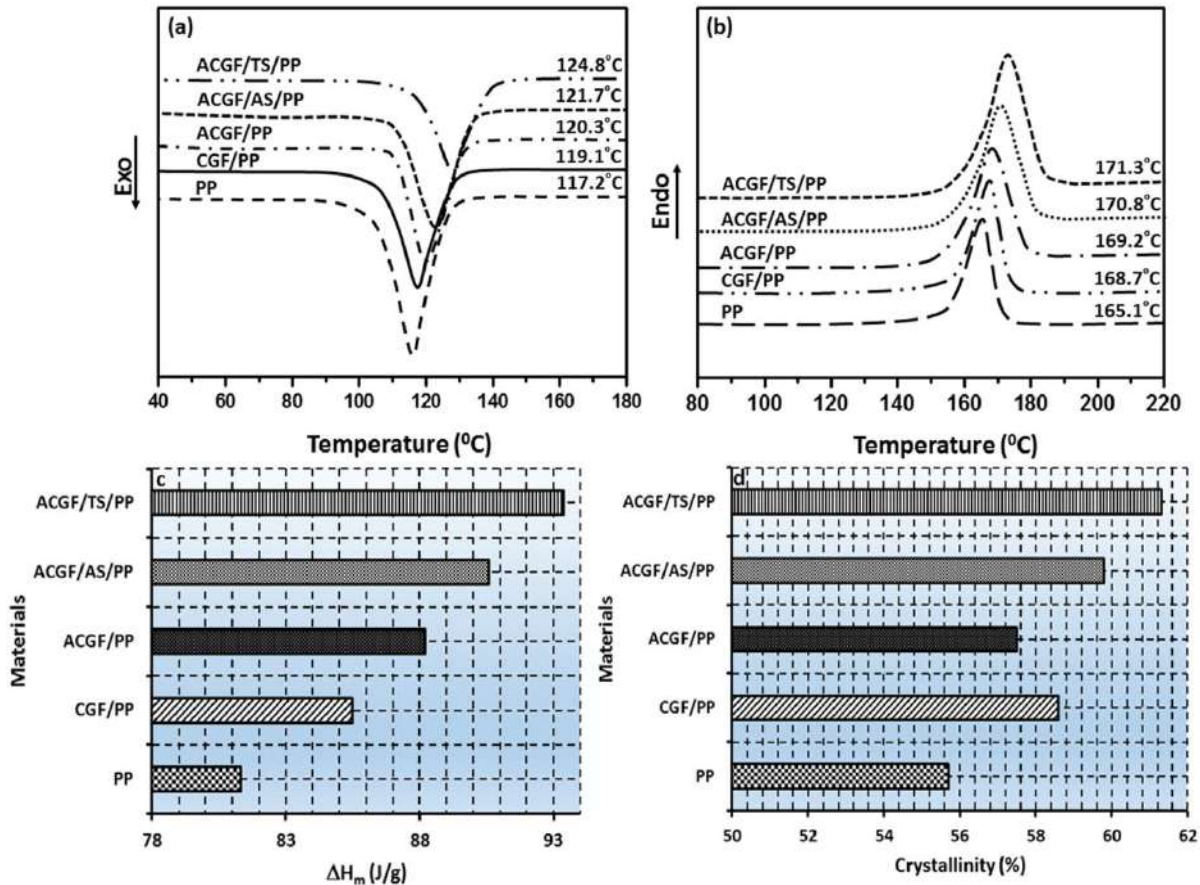

Figure 10: (a) DSC thermograms of CGF/PP, ACGF/PP, ACGF/AS/PP, and ACGF/TS/PP composites: (a) cooling cycle, (b) heating cycle, (c) melting enthalpy, and (d) crystallization behavior
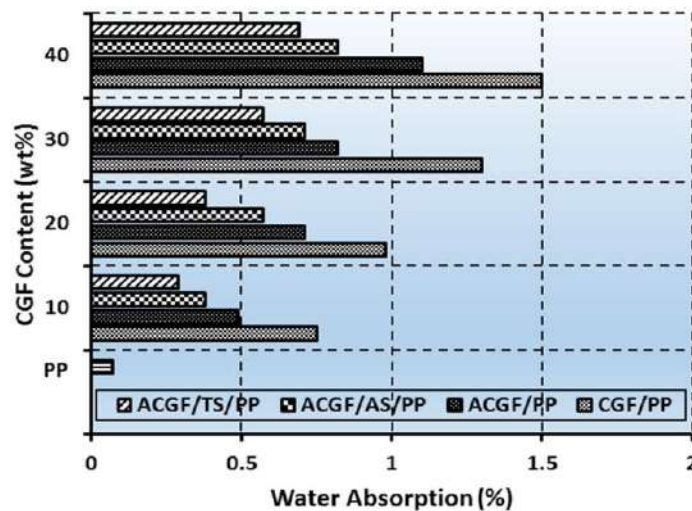

Figure 11: WA of CGF/PP, ACGF/PP, ACGF/AS/PP, and ACGF/TS/PP composites in different CGF contents

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CONCLUSIONS

The effects of chemical treatment (alkali and silane treatment) for CGF content on the fundamental properties of CGF/PP composites were investigated in this work. Following conclusions can be taken from research findings:

- As CGF content rose by 30 wt%, mechanical properties of CGF/PP composite samples, such as tensile strength, tensile modulus, impact strength, and hardness, improved. However, due to the CGF concentration, the tensile strength was decreased to 40%.
- The ACGF/AS/PP and ACGF/TS/PP composite samples outperformed control samples in terms of mechanical properties.
- SEM images show proof of enhanced mechanical, thermal, and WA characteristics of CGF/PP samples following silane treatment.
- Magnesium hydroxide was added to the ACGF/AS/PP and ACGF/TS/PP samples, which significantly reduced the combustion rate.
- The addition of CGF, AS, and TS resulted in a rise in T_c, T_m, and ΔH_m. The CGF's crystallization level is raised by adding AS and TS.
- Compared to the control composites, the WA of the treated composites was lower.

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